

# Design and selection of triazole-based compounds with high energetic properties and stabilities

GUOZHENG ZHAO\*, JIANFENG JIA and HAISHUN WU

School of Chemistry and Materials Science, Shanxi Normal University, Linfen,  
Shanxi, 041004, PR China  
e-mail: zhaoguo Zheng99@126.com

MS received 31 January 2016; revised 12 April 2016; accepted 25 May 2016

**Abstract.** Density functional theory (DFT) was used to study the molecular geometries, electronic structures, heats of formation in gas phase and in condensed phase, energetic properties, and thermal stabilities of triazole derivatives. The results show that the properties are associated with the different substituents and substitution positions in the parent ring. The symmetric structures and hyperconjugation systems both contribute to the thermal stabilities of the triazole derivatives. It is found that the group  $-N_3$  is an effective structural unit for improving the gas phase heat of formation. The calculated detonation properties indicate that  $-NO_2$ ,  $-ONO_2$ ,  $-N_3$ ,  $-NF_2$ , and  $-CH(NO_2)_2$  groups are very useful for enhancing the detonation velocities and detonation pressures. Thirteen compounds have better detonation properties than that of HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane). According to the quantitative data of energy and thermal stability for a nitrogen-rich high energetic compound, 20 out of 56 studied compounds may be considered as potential candidates with enhanced performance and reduced sensitivity.

**Keywords.** Density functional theory; triazole; heat of formation; energetics; thermal stability.

## 1. Introduction

To meet the continuing need for improved energy-rich compounds, extensive studies have been focused on nitrogen-rich high energetic compounds with decreased sensitivity and excellent energetic property.<sup>1–4</sup> Among various types of energy-rich compounds, triazole derivatives constitute a unique class of energetic compound and have received a substantial amount of interest due to their favorable insensitivity, good explosive performance, and environmental acceptability during the past two decades.<sup>5–8</sup>

As a triazole based compound, the most studied nitrotriazole explosive, 3-nitro-1,2,4-triazole-5-one (NTO) was reported by Becuwe and Delclos.<sup>9</sup> The crystal density of NTO is  $>1.90 \text{ g}\cdot\text{cm}^{-3}$ , and detonation pressure is equal to that of RDX (1,3,5-trinitro-1,3,5-triazinane).<sup>10,11</sup> 3-Amino-5-nitro-1,2,4-triazole (ANTA) is a more energetic alternative to NTO. It is reported that ANTA has a density of  $1.82 \text{ g}\cdot\text{cm}^{-3}$  and good thermal stability.<sup>12</sup> 4,6-Bis (5-amino-3-nitro-1,2,4-triazolyl)-5-nitropyrimidine (DANTNP) (M.p.  $330^\circ\text{C}$ ) is another insensitive explosive, which has a density of  $1.87 \text{ g}\cdot\text{cm}^{-3}$  and is slightly more powerful while its impact insensitivity is of the order of TATB (1,3,5-triamino-2,4,

6-trinitrobenzene).<sup>13</sup> Shreeve *et al.*,<sup>14</sup> synthesized a series of 1,2,4-triazole-linked energetic polynitropyrazoles, which showed that these compounds have potential applications as energetic compounds. Zhu *et al.*,<sup>15</sup> designed three novel explosives by introducing the *N*-oxides into the 1,2,4-triazole, which were more powerful than HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) and less sensitive than TNT (2,4,6-trinitrotoluene). Cheng *et al.*,<sup>16</sup> reported the synthesis and characterization of the chloride salt of 1,1'-(triaz-1-ene-1,3-diyl)bis(1*H*-tetrazol-5-amine), which contains an  $N_{11}$  structural adduct with 5-aminotetrazole.

Triazole has a nitrogen content of more than 60% and it is fascinating because of the three hydrogen atoms in the ring which can be replaced with functional groups.<sup>17–19</sup> It is well-known that the addition of energy-rich substituents, such as  $-NO_2$ ,  $-ONO_2$ ,  $-N_3$ ,  $-NF_2$ , and  $-CH(NO_2)_2$ , create exceptionally powerful explosives, propellants, and fuels with excellent explosive properties. Highly accurate *ab initio* and density functional theory (DFT) methods predict quantitatively energetic properties, such as density, detonation velocity, detonation pressure, and thermal stability.<sup>20,21</sup> These methods have been adopted to investigate structure and related properties, and select the most promising nitrogen-rich, high energetic compounds for laboratory synthesis and further consideration.<sup>22,23</sup>

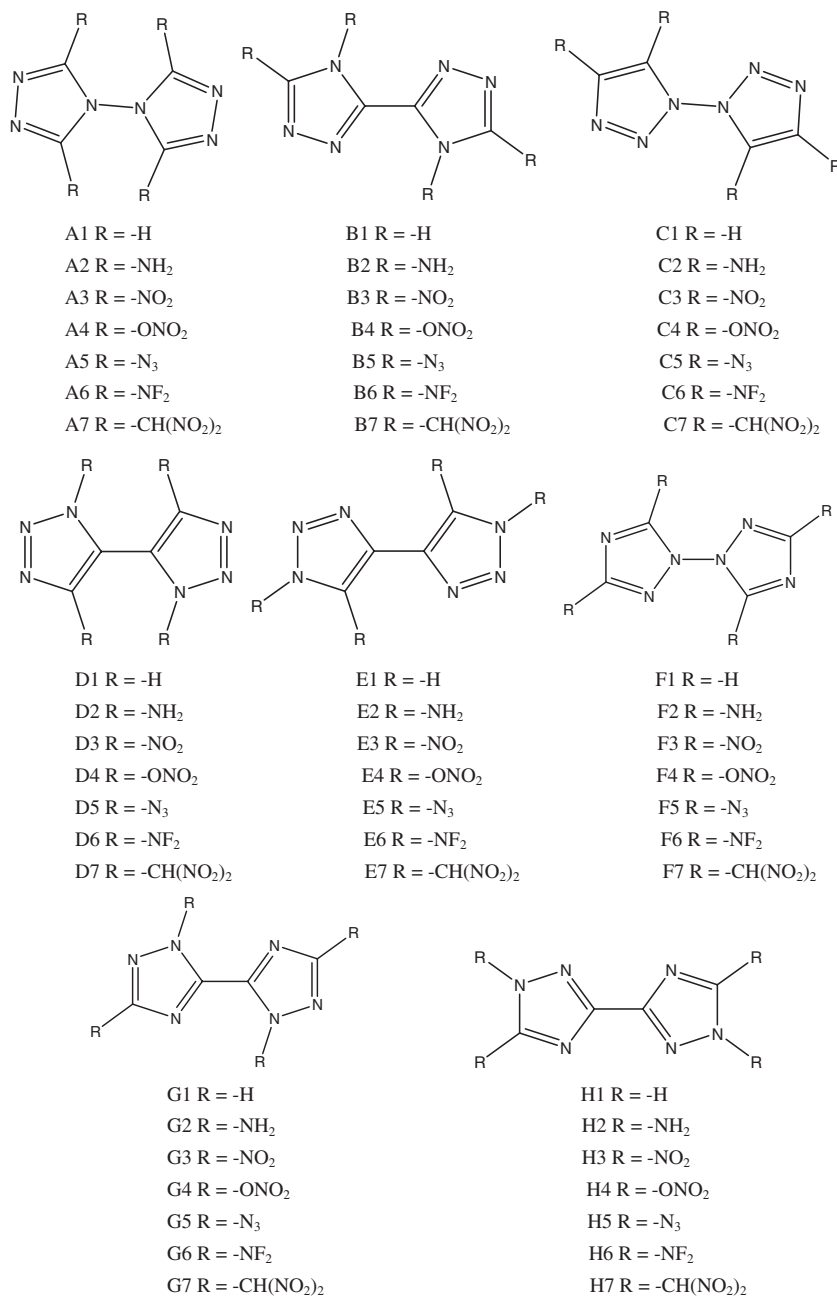
\*For correspondence

In this work, a systematic study was done on the optimized structures, heats of formation in gas phase and in condensed phase, energetic properties, and thermal stabilities of the triazole derivatives by using the DFT method. The main purpose here was to investigate the roles of different substituents and select new triazole-based high energetic compounds. First, 56 triazole derivatives were designed and optimized. Then, the heats of formation in gas phase were calculated *via* designed isodesmic reactions. The condensed phase heats of formation can be obtained from the gas phase heats of formation and heats of sublimation. In addition, the detonation velocities and pressures were predicted

using the calculations of condensed phase heats of formation and theoretical densities. Finally, the thermal stabilities were evaluated based on the bond dissociation energies.

## 2. Computational methods

The molecular frameworks of triazole-based compounds (molecular numbering as A1-A7, B1-B7, C1-C7, D1-D7, E1-E7, F1-F7, G1-G7, and H1-H7) are presented in figure 1. Geometry optimization for triazole derivatives were performed at the B3LYP/6-311G(d,p) level of



**Figure 1.** Frameworks of triazole-based compounds.

theory using the Gaussian software package.<sup>24</sup> The theoretical density was obtained using an improved equation proposed by Politzer *et al.*,<sup>25</sup> in which the intermolecular interactions were taken into account *via* the electrostatic interactions on the molecular surface.

$$\rho = \alpha \left[ \frac{M}{V(0.001)} \right] + \beta (\nu\sigma_{\text{tot}}^2) + \gamma \quad (1)$$

where,  $M$  is molecular mass in  $\text{g}\cdot\text{molecule}^{-1}$  and  $V(0.001)$  is volume in  $\text{cm}^3\cdot\text{molecule}^{-1}$ , which is encompassed by the 0.001 e-Bohr<sup>-3</sup> contour of the molecule's electronic density;  $\alpha$ ,  $\beta$  and  $\gamma$  are the regression coefficients;  $\nu$  is a measure of the degree of balance between positive potential and negative potential on the isosurface, and  $\sigma_{\text{tot}}^2$  describes the variability of electronic potential on molecular surface.

DFT-B3LYP method<sup>26,27</sup> with 6-311G(d,p) basis set was adopted for prediction of the heat of formation (HOF) in gas phase *via* designing isodesmic reaction at 298 K. The isodesmic reaction method was employed successfully to calculate gas phase heats of formation ( $\Delta_f H_{\text{Gas}}^0$ ) of many organic compounds from the total energies with the help of density functional theory calculations.<sup>28,29</sup> In the isodesmic reactions, the aza cyclic skeletons of triazole derivatives are kept invariable. The heat of reaction ( $\Delta H_{298}$ ) was calculated by the following equation:

$$\begin{aligned} \Delta H_{298} &= \sum \Delta H_{f,P} - \sum \Delta H_{f,R} \\ &= \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (2) \end{aligned}$$

where,  $\Delta H_{f,R}$  and  $\Delta H_{f,P}$  are the  $\Delta_f H_{\text{Gas}}^0$  of reactants and products at 298 K, respectively;  $\Delta E_0$  and  $\Delta ZPE$  are the differences between the total energies at 0 K and between the zero-point vibrational energies of products and reactants, respectively;  $\Delta H_T$  is thermal correction from 0 K to 298 K;  $\Delta nRT$  is work term.

Equation (3) was used to calculate the condensed phase heat of formation ( $\Delta_f H_{\text{Cond}}^0$ ) from the  $\Delta_f H_{\text{Gas}}^0$  and the heat of sublimation ( $\Delta H_{\text{Sub}}^0$ ).<sup>30</sup>

$$\Delta_f H_{\text{Cond}}^0 = \Delta_f H_{\text{Gas}}^0 - \Delta H_{\text{Sub}} \quad (3)$$

Here,  $\Delta H_{\text{Sub}}$  is the heat of sublimation estimated using Equation (4) suggested by Rice *et al.*<sup>31</sup> and Polizer *et al.*:<sup>32</sup>

$$\Delta H_{\text{Sub}} = \beta_1(SA)^2 + \beta_2(\nu\sigma_{\text{tot}}^2)^{0.5} + \beta_3 \quad (4)$$

where,  $SA$  is the surface area of 0.001 e-bohr<sup>-3</sup> isosurface of electronic density;  $\nu$  is a measure of the degree of balance between positive potential and negative potential on the isosurface;  $\sigma_{\text{tot}}^2$  describes the variability of electronic potential on molecular surface;  $\beta_1$ ,

$\beta_2$ , and  $\beta_3$  are the correlation coefficients taken from Ref.<sup>33</sup>

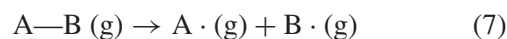
Detonation velocity and detonation pressure were calculated by the Kamlet-Jacobs equations<sup>34,35</sup> as:

$$P = 1.558NM^{1/2}Q^{1/2}\rho^2 \quad (5)$$

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (6)$$

where, each term in Equations (5) and (6) is defined as follows:  $P$ , the detonation pressure (GPa);  $D$ , the detonation velocity ( $\text{km}\cdot\text{s}^{-1}$ );  $N$ , the number moles of detonation gases per gram of explosive;  $M$ , the average molecular weight of detonation gases;  $Q$ , the energy of explosion ( $\text{cal}\cdot\text{g}^{-1}$ );  $\rho$ , the crystal density ( $\text{g}\cdot\text{cm}^{-3}$ ).

The thermal stability was investigated by evaluating the bond dissociation energy (BDE).<sup>36,37</sup> In the present study, the BDEs of relatively weak bonds of the triazole derivatives were evaluated using the following equation:



$$\text{BDE(A—B)}_{\text{ZPE}} = E(\text{A}\cdot)_{\text{ZPE}} + E(\text{B}\cdot)_{\text{ZPE}} - E(\text{A—B})_{\text{ZPE}} \quad (8)$$

where A—B stands for the neutral molecule and A· and B· for the corresponding product radicals of the dissociation of the A—B bond;  $\text{BDE(A—B)}$  is the BDE of bond A—B;  $E(\text{A—B})_{\text{ZPE}}$ ,  $E(\text{A}\cdot)_{\text{ZPE}}$  and  $E(\text{B}\cdot)_{\text{ZPE}}$  are their corresponding total energies corrected by the zero-point vibrational energies of parent compound and corresponding radicals, respectively.

### 3. Results and Discussion

#### 3.1 Molecular geometry and electronic structure

Optimized bond lengths of triazole derivatives are tabulated in table 1. For A1, B1, C1, D1, E1, F1, G1, and H1, the bond lengths and bond angles of the triazole ring in the ring skeleton are close to those of corresponding compounds. It shows that the substitution of the groups do not affect the bond lengths and bond angles in the triazole ring skeleton significantly. It is proposed that all the C—N bonds lengths in ring skeleton of triazole derivatives are between 1.2928 Å and 1.4142 Å, which are much shorter than normal C—N single bond that is referred to 1.49 Å.<sup>38</sup> All the atoms in the parent structure are in a hyperconjugation system, which can delocalize  $\pi$  electron cloud density of system. Consequently, it can be concluded that the hyperconjugation system contributes to the stability of triazole derivatives.

**Table 1.** Bond lengths of triazole derivatives computed at B3LYP/6-311G(d,p) level.

Compd.	Bond	Length(Å)	Bond	Length(Å)	Bond	Length(Å)	Bond	Length(Å)
A1	C1–N3	1.3747	N3–N8	1.3843	N11–N12	1.3790	N13–N14	1.3790
A2	C1–N3	1.4142	N3–N6	1.4357	N7–N8	1.3737	C1–N20	1.3889
A3	C1–N3	1.3948	N3–N6	1.4107	N7–N8	1.3677	C1–N14	1.4720
A4	C1–N3	1.4101	N3–N6	1.4062	C1–O13	1.3059	O13–N17	1.6670
A5	C1–N3	1.3855	N3–N6	1.3602	C1–N13	1.3813	N17–N21	1.1252
A6	C1–N3	1.3997	N3–N6	1.4146	C1–N14	1.4266	N14–F21	1.3975
A7	N3–N6	1.4210	N7–N8	1.3513	C1–C17	1.4884	C17–N40	1.5352
B1	C2–N3	1.3641	C2–C6	1.4436	N11–N12	1.3769	N13–N14	1.3771
B2	C2–N3	1.3948	C2–C4	1.4672	N7–N8	1.3766	C1–N14	1.3905
B3	C2–N3	1.3789	C2–C4	1.4489	C1–N14	1.4626	N3–N13	1.4619
B4	C2–C4	1.4531	N7–N8	1.3752	C1–O14	1.3149	O14–N18	1.6445
B5	C2–C4	1.4556	N7–N8	1.3797	C1–N14	1.3828	N3–N13	1.4043
B6	C2–C4	1.4666	C1–N12	1.4279	N3–N11	1.3897	N11–F20	1.3939
B7	C2–C4	1.4535	C1–C11	1.4856	N3–C13	1.4267	C11–N20	1.5421
C1	C2–N3	1.3571	N6–N7	1.3003	N3–N10	1.3736	N13–N14	1.3003
C2	C2–C3	1.3584	N3–N8	1.3759	N4–N5	1.2970	C1–N14	1.4110
C3	N3–N8	1.3734	N4–N5	1.2874	C1–N14	1.4562	C2–N13	1.4747
C4	N3–N8	1.3545	C1–O14	1.3343	C2–O13	1.3085	O14–N18	1.5868
C5	N3–N8	1.3545	N4–N5	1.2863	C1–N14	1.3914	C2–N13	1.3772
C6	N3–N8	1.3777	C1–N12	1.4279	C2–N11	1.4234	N11–F19	1.4103
C7	N3–N8	1.3597	N4–N5	1.2836	C1–C17	1.4913	C2–C15	1.4817
D1	C2–N3	1.3620	C2–C6	1.4434	N3–N11	1.3475	N11–N12	1.2988
D2	C1–C2	1.4086	C2–C4	1.4581	N3–N7	1.3330	C1–N17	1.3784
D3	C1–N8	1.3498	C2–C4	1.4530	C1–N14	1.4592	N3–N11	1.5475
D4	C2–C4	1.4449	N3–N7	1.3570	C1–O14	1.3369	O14–N18	1.5715
D5	C2–C4	1.4393	C1–N14	1.3921	N3–N11	1.3948	N15–N19	1.1248
D6	C2–C4	1.4566	C1–N13	1.4298	N3–N11	1.3955	N11–F17	1.3904
D7	C2–C4	1.4533	C1–C17	1.4850	N3–C11	1.4247	C11–N19	1.5482
E1	C1–C2	1.3781	C1–N3	1.3539	C2–C6	1.4499	N3–N11	1.3480
E2	C1–C2	1.3892	C2–C4	1.4426	C1–N14	1.3651	N3–N11	1.3903
E3	C2–C4	1.4458	N3–N7	1.3484	C1–N11	1.4670	N3–N12	1.4948
E4	C2–C4	1.4387	C1–O12	1.3076	N3–O11	1.3190	O11–N15	1.6429
E5	C2–C4	1.4469	C1–N12	1.3810	N3–N11	1.3907	N11–N15	1.2486
E6	C2–C4	1.4504	C1–N12	1.4170	N3–N11	1.3963	N11–F15	1.3903
E7	C2–C4	1.4489	C1–C15	1.4787	N3–C17	1.4237	C11–N22	1.5473
F1	C1–N6	1.3253	C2–N7	1.3192	N3–N6	1.3469	N3–N10	1.3751
F2	C2–N3	1.3579	N3–N8	1.3821	C1–N20	1.3775	C2–N11	1.3573
F3	C1–N5	1.3490	N3–N8	1.3776	C1–N13	1.4757	C2–N14	1.4769
F4	N3–N8	1.3577	C1–O14	1.3441	C2–O13	1.3159	O11–N15	1.5435
F5	N3–N8	1.3533	C1–N13	1.3897	C2–N12	1.3772	N11–N15	1.2420
F6	N3–N8	1.3818	C1–N14	1.4324	C2–N11	1.4313	N11–F17	1.4116
F7	N3–N8	1.3626	C1–C17	1.4870	C2–C15	1.4858	C11–N19	1.5345
G1	C1–N6	1.3240	C2–C8	1.4457	N3–N6	1.3503	C8–N14	1.3247
G2	C1–N5	1.3586	C2–C6	1.4533	C1–N20	1.3795	N3–N11	1.3916
G3	C1–N4	1.3179	C2–C6	1.4497	C1–N12	1.4736	N3–N11	1.5541
G4	C2–C6	1.4461	C1–O12	1.3423	N3–O11	1.3196	O11–N15	1.6481
G5	C2–C6	1.4476	C1–N14	1.3900	N3–N11	1.3902	N15–N19	1.1290
G6	C2–C6	1.4551	C1–N14	1.4333	N3–N11	1.3896	N11–F21	1.3939
G7	C2–C6	1.4488	C1–C13	1.4852	N3–C11	1.4199	C11–N25	1.5419
H1	C1–N3	1.3522	C2–N6	1.3275	C2–C9	1.4621	C8–N10	1.3522
H2	C1–N3	1.3628	C2–C7	1.4621	N3–N4	1.3652	C1–N20	1.3831
H3	C1–N3	1.3677	C2–C7	1.4589	C1–N12	1.4709	N3–N13	1.5006
H4	C1–N3	1.3835	C2–C7	1.4590	C1–O12	1.3207	O12–N16	1.6204
H5	C1–N3	1.3650	C2–C7	1.4583	C1–N14	1.3818	N15–N19	1.1291
H6	C1–N3	1.3686	C1–N14	1.4302	N3–N11	1.3908	N11–F15	1.3916
H7	C2–C7	1.4598	C1–C13	1.4930	N3–C11	1.4147	C11–N19	1.5448

It can be seen from table 1 that the introduction of the  $-\text{NH}_2$ ,  $-\text{NO}_2$ ,  $-\text{ONO}_2$ ,  $-\text{N}_3$ ,  $-\text{NF}_2$ , and  $-\text{CH}(\text{NO}_2)_2$  groups produce some influences on the geometric parameters of the central ring for each series. For B series, the bond lengths and bond angles in the central ring for the substituted derivatives change slightly compared to the parent compound (B1). For B1, the dihedral angles related to the central ring skeleton such as  $\text{N8}-\text{C6}-\text{C2}-\text{N12}$ ,  $\text{C6}-\text{N13}-\text{N14}-\text{C7}$ ,  $\text{C1}-\text{N3}-\text{C2}-\text{C6}$  and  $\text{N3}-\text{C1}-\text{N11}-\text{N12}$  equal to  $0^\circ$  or  $180^\circ$ . The groups attached to central ring skeleton are repulsed, which make them out of plane. The same is true of series A, C, D, E, F, G, and H. In addition, the  $\text{C}-\text{NO}_2$  bond lengths of all the  $-\text{NO}_2$  substituted derivatives are in the range of 1.4562–1.4759 Å, which are also shorter than normal  $\text{C}-\text{N}$  single bond that is referred to 1.49 Å,<sup>38</sup> suggesting that the  $\text{C}-\text{NO}_2$  bonds in triazole derivatives participate in the hyperconjugation system. By analyzing the structures of triazole derivatives, it is easy to find that triazole derivatives are symmetric structures, which make thermal stabilities of triazole derivatives increase. Therefore, it may be inferred that triazole derivatives have good thermal stability and low sensitivity.

Energies (a.u.) of frontier molecular orbitals and their gaps ( $\Delta E_{\text{LUMO}-\text{HOMO}}$ ) of triazole derivatives at B3LYP/6-311G(d,p) level are listed in table 2. For the triazole derivatives, when the  $-\text{NH}_2$  and  $-\text{N}_3$  groups are attached to the ring, the HOMO energies increase, whereas attaching other groups such as  $-\text{NO}_2$ ,  $-\text{ONO}_2$ ,  $-\text{NF}_2$ , and  $-\text{CH}(\text{NO}_2)_2$  decrease the HOMO energies. All the title compounds with the substituents  $-\text{NO}_2$ ,  $-\text{ONO}_2$ ,  $-\text{N}_3$ ,  $-\text{NF}_2$ , and  $-\text{CH}(\text{NO}_2)_2$  have lower LUMO energies than the corresponding unsubstituted compounds, whereas those with the  $-\text{NH}_2$  group have higher LUMO energies. This shows that different substituents exert different effects on the HOMO and LUMO energies of the triazole derivatives. This case is consistent with that of the energy gaps ( $\Delta E_{\text{LUMO}-\text{HOMO}}$ ). All the substituted derivatives have smaller HOMO–LUMO gaps than the corresponding unsubstituted compounds, which reflect a shift toward lower frequencies in their electronic absorption spectra. Among the derivatives, the  $\Delta E_{\text{LUMO}-\text{HOMO}}$  of A1 (0.22816 a.u.) is the largest while E4 is the smallest (0.13184 a.u.). Overall, comparing differently substituted compounds leads to a comparison of the energetics.

### 3.2 Heats of formation (HOF)

HOF is usually taken as the indicator of the ‘energy content’ of a energy-rich compound. Therefore, it is very important to predict HOF accurately. Table 3 lists the electronic energies, zero-point energies, thermal

**Table 2.** Energy of highest occupied molecular orbital ( $E_{\text{HOMO}}$ ), energy of lowest unoccupied molecular orbital ( $E_{\text{LUMO}}$ ) and energy gaps ( $\Delta E_{\text{LUMO}-\text{HOMO}}$ ) for the triazole derivatives.

Compound	HOMO (a.u.)	LUMO (a.u.)	$\Delta E_{\text{LUMO}-\text{HOMO}}$ (a.u.)
A1	−0.28572	−0.05756	0.22816
A2	−0.22590	−0.01433	0.21157
A3	−0.35142	−0.18899	0.16243
A4	−0.29339	−0.14733	0.14606
A5	−0.25753	−0.07461	0.18292
A6	−0.32264	−0.14324	0.17940
A7	−0.34532	−0.17453	0.17079
B1	−0.25709	−0.04869	0.20840
B2	−0.21112	−0.02426	0.18686
B3	−0.31957	−0.18680	0.13277
B4	−0.28815	−0.13812	0.15003
B5	−0.25294	−0.11619	0.13675
B6	−0.31302	−0.13718	0.17584
B7	−0.33096	−0.16028	0.17068
C1	−0.28329	−0.06648	0.21681
C2	−0.21706	−0.02608	0.19098
C3	−0.35269	−0.15363	0.19906
C4	−0.29882	−0.14110	0.15772
C5	−0.24953	−0.09594	0.15359
C6	−0.32537	−0.13850	0.18687
C7	−0.33847	−0.16184	0.17663
D1	−0.26201	−0.06612	0.19589
D2	−0.19210	−0.04284	0.14926
D3	−0.32394	−0.17752	0.14642
D4	−0.28857	−0.14592	0.14265
D5	−0.24898	−0.09734	0.15164
D6	−0.31286	−0.14983	0.16303
D7	−0.34326	−0.15512	0.18814
E1	−0.23997	−0.02016	0.21981
E2	−0.18427	0.00251	0.18678
E3	−0.30808	−0.15135	0.15673
E4	−0.26760	−0.13576	0.13184
E5	−0.23786	−0.09813	0.13973
E6	−0.31641	−0.12751	0.18890
E7	−0.31643	−0.14775	0.16868
F1	−0.27712	−0.05594	0.22118
F2	−0.19085	0.01096	0.20181
F3	−0.34457	−0.15271	0.19186
F4	−0.30923	−0.13175	0.17748
F5	−0.26797	−0.09188	0.17609
F6	−0.32913	−0.13016	0.19897
F7	−0.34715	−0.15013	0.19702
G1	−0.26343	−0.05986	0.20357
G2	−0.21011	−0.03258	0.17753
G3	−0.33076	−0.15331	0.17745
G4	−0.29518	−0.13338	0.16180
G5	−0.25210	−0.09452	0.15758
G6	−0.31929	−0.13401	0.18528
G7	−0.33158	−0.15159	0.17999
H1	−0.24655	−0.01954	0.22701
H2	−0.20786	−0.00340	0.20446
H3	−0.31916	−0.15064	0.16852
H4	−0.27550	−0.12315	0.15235
H5	−0.24049	−0.09157	0.14892
H6	−0.32202	−0.11565	0.20637
H7	−0.31829	−0.14580	0.17249



**Table 3.** Calculated electronic energies ( $E_0$ ), zero-point energies (ZPE), thermal corrections to enthalpy ( $H_T$ ) and gas phase heats of formation of the reference compounds.<sup>a</sup>

Compound	$E_0$ (a.u.)	ZPE (a.u.)	$H_T$ (kJ·mol <sup>-1</sup> )	HOF (kJ·mol <sup>-1</sup> )
CH <sub>4</sub>	-40.4891	0.0437	9.61	-74.60 <sup>b</sup>
CH <sub>3</sub> CH <sub>3</sub>	-79.7819	0.0729	11.16	-84.00 <sup>b</sup>
CH <sub>3</sub> NH <sub>2</sub>	-95.8246	0.0625	10.96	-22.50 <sup>b</sup>
CH <sub>3</sub> NO <sub>2</sub>	-245.0319	0.0488	13.17	-80.80 <sup>b</sup>
CH <sub>3</sub> ONO <sub>2</sub>	-320.2174	0.0524	13.53	-124.40 <sup>b</sup>
CH <sub>3</sub> N <sub>3</sub>	-204.0982	0.0492	13.65	296.50 <sup>c</sup>
CH <sub>3</sub> NF <sub>2</sub>	-294.2516	0.0459	13.06	-114.78 <sup>c</sup>
4 <i>H</i> -1,2,4-triazole	-242.2438	0.0577	11.50	217.93 <sup>d</sup>
1 <i>H</i> -1,2,3-triazole	-242.2270	0.0577	11.43	267.03 <sup>d</sup>
1 <i>H</i> -1,2,4-triazole	-242.2537	0.0585	11.32	193.45 <sup>d</sup>

<sup>a</sup> The scaling factor is 0.98 for the ZPE and 0.96 for  $H_T$ .<sup>39</sup>

<sup>b</sup> The experimental HOFs were taken from Ref.<sup>40-42</sup> respectively.

<sup>c</sup> The theoretical HOFs were taken from Ref.<sup>43</sup>

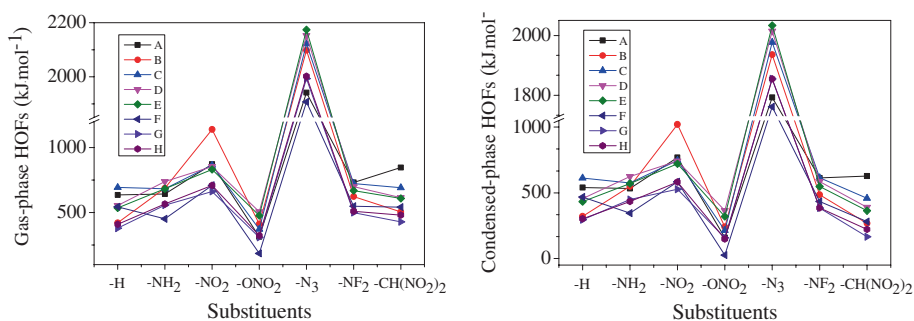
<sup>d</sup> The theoretical HOFs were taken from Ref.<sup>44</sup>

corrections, and gas phase heats of formation for the reference compounds in the isodesmic reactions. Figure 2 displays the comparison of the HOFs of triazole derivatives with different substituents. The isodesmic reaction was used to derive the gas phase heat of formation  $\Delta_f H_{\text{Gas}}^{\circ}$  of triazole derivatives at 298 K (scheme 1).

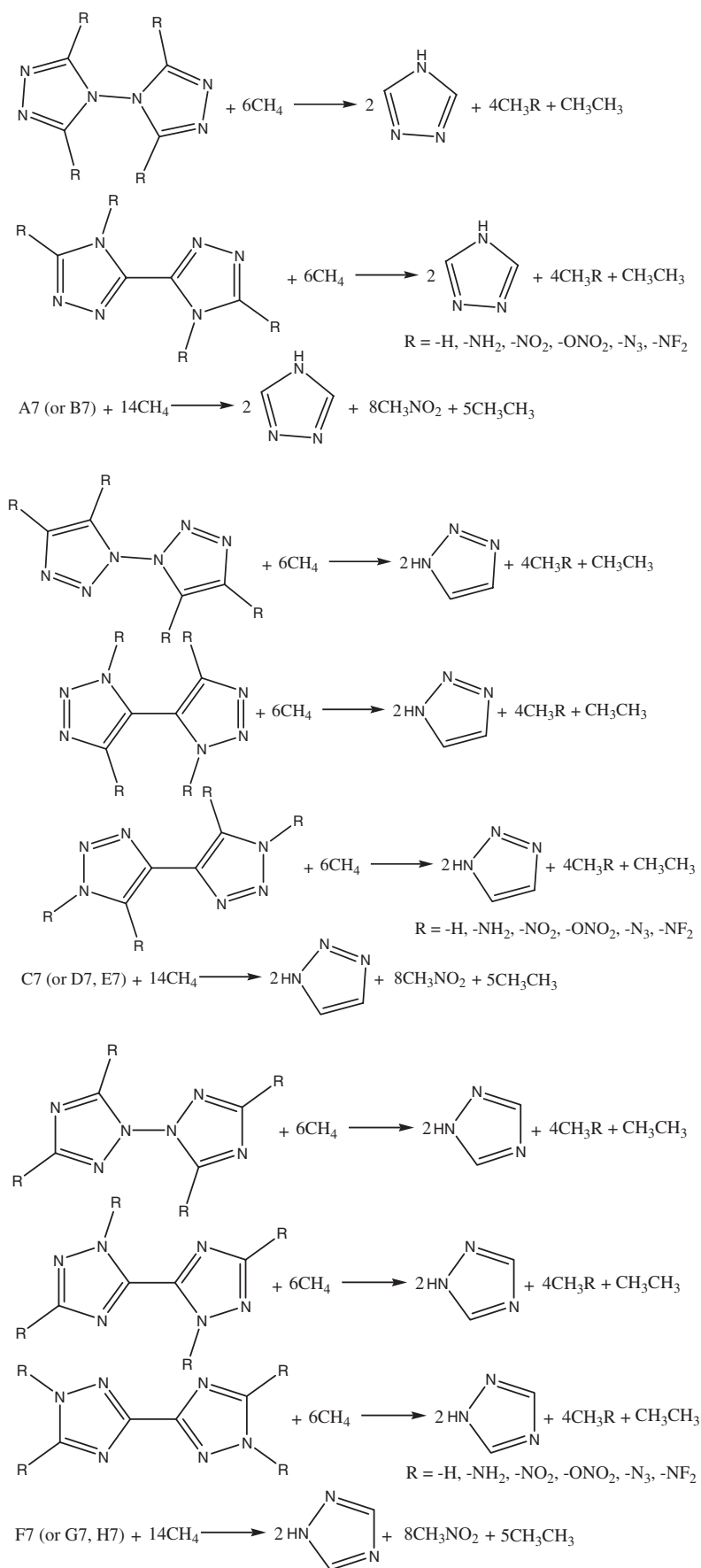
Table 4 presents the total energies, ZPEs, thermal corrections, molecular properties, and gas phase and condensed phase heats of formation of the triazole derivatives. The effects of different substituents on the gas phase and condensed phase heats of formation of the triazole derivatives were investigated. For the A series, when the substituents are -NH<sub>2</sub>, -NO<sub>2</sub>, -N<sub>3</sub>, -NF<sub>2</sub>, and -CH(NO<sub>2</sub>)<sub>2</sub>, the  $\Delta_f H_{\text{Gas}}^{\circ}$  of A2, A3, A5, A6, A7 increase compared with the unsubstituted case (A1), whereas the opposite is true for the substituent -ONO<sub>2</sub>. This also holds for the B, D, E, G, and H series. However, for the C and F series, the situation is different. The substitution of -NO<sub>2</sub>, -N<sub>3</sub> or -NF<sub>2</sub> increases the  $\Delta_f H_{\text{Gas}}^{\circ}$  values of C3, C5, C6, F3, F5

and F6, respectively, while the substitution of -NH<sub>2</sub>, -ONO<sub>2</sub> or -CH(NO<sub>2</sub>)<sub>2</sub> has the opposite effect. -N<sub>3</sub> substituted derivatives have the largest  $\Delta_f H_{\text{Gas}}^{\circ}$  values ( $\Delta_f H_{\text{Gas}}^{\circ} > 1900$  kJ·mol<sup>-1</sup>) than the other substituted ones in the series. In addition, substitution of the group -ONO<sub>2</sub> greatly decreases the  $\Delta_f H_{\text{Gas}}^{\circ}$  values compared with those of the unsubstituted compounds. This shows that the substitution of -N<sub>3</sub> is helpful for increasing the gas phase heats of formation of the triazole derivatives, while substituting -ONO<sub>2</sub> greatly reduces  $\Delta_f H_{\text{Gas}}^{\circ}$  values.

From figure 2, it was found that, qualitatively, the calculated condensed phase heats of formation ( $\Delta_f H_{\text{Cond}}^{\circ}$ ) show the same trend as the gas phase heats of formation ( $\Delta_f H_{\text{Gas}}^{\circ}$ ). This shows that the trend in the heats of formation of the triazole derivatives observed when the substituents are varied, is similar for the compounds in the gas phase and for those in the condensed phase. As shown in table 4, among the 56 triazole derivatives, 28 molecules possess a  $\Delta_f H_{\text{Cond}}^{\circ}$  values  $> 500$  kJ·mol<sup>-1</sup>.



**Figure 2.** Comparison of the HOFs of triazole derivatives with different substituents.



**Scheme 1.** The isodesmic reactions of triazole derivatives.

**Table 4.** Calculated total energies ( $E_0$ , a.u.), zero-point energies (ZPE, a.u.), thermal corrections ( $H_T$ , kJ·mol<sup>-1</sup>), molecular properties, heats of sublimation (kJ·mol<sup>-1</sup>), and heats of formation (kJ·mol<sup>-1</sup>) for the triazole derivatives.<sup>a</sup>

Compd	$E_0$	ZPE	$H_T$	$\Delta_f H_{\text{Gas}}^{\circ}$	SA	$\nu$	$\sigma_{\text{tot}}^2$	$\Delta H_{\text{Sub}}$	$\Delta_f H_{\text{Cond}}^{\circ}$
A1	-483.2415	0.0950	18.3936	635.39	157.40	0.24	264.19	95.47	539.92
A2	-704.6623	0.1636	30.5280	643.56	200.13	0.23	270.22	111.45	532.11
A3	-1301.3172	0.1030	43.1040	871.75	244.02	0.06	214.40	103.13	768.62
A4	-1602.2100	0.1156	57.3984	314.30	293.95	0.25	179.32	155.02	159.28
A5	-1137.7511	0.1075	48.1536	1941.77	294.61	0.22	152.12	149.23	1792.54
A6	-1498.1996	0.0899	47.3088	730.85	247.25	0.10	294.22	118.47	612.38
A7	-2276.6531	0.2225	84.3744	847.05	408.11	0.04	275.66	220.36	626.69
B1	-483.3237	0.0970	20.3232	421.49	157.99	0.25	307.96	100.58	320.91
B2	-704.6459	0.1614	31.6608	687.78	211.65	0.22	552.39	138.76	549.02
B3	-1301.2161	0.0992	44.9952	1139.11	250.33	0.11	270.91	119.57	1019.54
B4	-1602.1736	0.1162	59.7504	412.45	306.80	0.25	248.74	172.09	240.36
B5	-1137.6918	0.1052	48.8544	2098.32	289.00	0.25	275.81	162.70	1935.62
B6	-1498.2412	0.0895	48.6624	622.99	256.26	0.21	271.24	137.84	485.15
B7	-2276.7842	0.2245	86.7744	505.41	419.62	0.07	229.44	237.63	267.78
C1	-483.2232	0.0949	18.0960	693.09	158.34	0.24	142.50	80.92	612.17
C2	-704.6522	0.1605	33.3600	683.17	210.24	0.25	180.68	108.20	574.97
C3	-1301.3250	0.1023	45.6000	864.07	262.79	0.07	259.62	118.93	745.14
C4	-1602.1932	0.1158	60.2688	371.71	313.89	0.19	141.47	158.71	213.00
C5	-1137.6866	0.1056	48.8640	2121.92	282.68	0.23	171.01	145.26	1976.66
C6	-1498.2066	0.0893	48.6336	724.04	256.31	0.08	170.50	110.63	613.41
C7	-2276.7173	0.2237	86.8800	691.35	411.67	0.07	280.71	232.99	458.36
D1	-483.2759	0.0962	18.5280	555.41	158.27	0.20	361.97	99.30	456.11
D2	-704.6304	0.1631	31.7088	738.81	203.33	0.25	264.69	114.77	624.04
D3	-1301.3288	0.1022	46.3872	854.74	246.66	0.15	154.53	113.19	741.55
D4	-1602.1406	0.1160	56.7264	506.13	293.07	0.21	110.44	141.35	364.78
D5	-1137.6747	0.1055	48.4704	2152.77	285.57	0.25	101.49	138.35	2014.42
D6	-1498.2155	0.0897	47.4528	699.43	250.18	0.11	202.75	114.32	585.11
D7	-2276.7465	0.2236	87.0912	614.86	409.18	0.05	284.28	224.94	389.92
E1	-483.2841	0.0968	20.3232	535.75	158.14	0.23	355.45	102.68	433.07
E2	-704.6525	0.1626	34.6176	683.76	211.29	0.25	221.94	113.73	570.03
E3	-1301.3376	0.1018	46.1664	831.53	264.40	0.12	162.26	110.48	721.05
E4	-1602.1531	0.1159	60.0384	476.74	311.24	0.20	136.05	156.36	320.38
E5	-1137.6668	0.1052	49.5168	2174.52	285.74	0.25	118.76	141.15	2033.37
E6	-1498.2273	0.0895	48.1920	669.29	260.12	0.18	126.07	121.34	547.95
E7	-2276.7488	0.2241	86.9280	608.46	425.47	0.06	338.90	244.64	363.82
F1	-483.2773	0.0965	17.8656	544.56	157.71	0.23	121.20	76.53	468.03
F2	-704.7377	0.1624	32.7072	451.59	210.75	0.24	172.92	106.69	344.90
F3	-1301.3817	0.1037	45.8304	709.12	270.63	0.09	224.41	125.68	583.44
F4	-1602.2612	0.1181	59.2224	185.69	324.51	0.16	116.68	159.62	26.07
F5	-1137.7653	0.1077	47.6256	1907.71	287.58	0.23	155.13	146.08	1761.63
F6	-1498.2710	0.0911	48.1248	548.23	260.81	0.07	190.82	113.39	434.84
F7	-2276.7722	0.2240	88.3008	542.11	445.78	0.06	253.31	260.79	281.32
G1	-483.3410	0.0984	20.0352	379.62	157.72	0.21	194.58	84.70	294.92
G2	-704.6985	0.1631	36.0288	557.48	216.78	0.25	166.66	109.52	447.96
G3	-1301.4008	0.1030	48.3936	661.60	269.77	0.17	201.77	134.33	527.27
G4	-1602.2139	0.1181	58.6368	309.31	318.16	0.16	84.02	151.03	158.28
G5	-1137.7330	0.1068	48.0864	1993.09	291.65	0.25	81.15	138.33	1854.76
G6	-1498.2905	0.0913	50.1504	498.93	264.75	0.08	160.97	115.02	383.91
G7	-2276.8150	0.2251	87.2544	428.90	441.94	0.09	248.78	263.23	165.67
H1	-483.3293	0.0978	20.2368	410.53	158.30	0.25	383.57	107.96	302.57
H2	-704.6951	0.1632	34.7904	565.59	218.82	0.23	378.85	130.84	434.75
H3	-1301.3974	0.1033	47.8560	709.12	271.65	0.14	153.68	126.62	582.50
H4	-1602.2090	0.1174	59.4144	322.94	321.73	0.23	184.84	173.55	149.39
H5	-1137.7299	0.1064	49.1136	2002.18	294.68	0.23	128.47	147.17	1855.01
H6	-1498.2861	0.0910	50.3328	510.82	267.37	0.17	135.73	125.98	384.84
H7	-2276.7950	0.2246	87.1008	481.18	439.74	0.06	324.80	259.24	221.94

<sup>a</sup> The scaling factor is 0.98 for ZPE and 0.96 for  $H_T$ .<sup>39</sup>  $U(\text{SA}) = 0.01 \text{ \AA}^2$ ,  $U(\sigma_{\text{tot}}^2) = 0.01 \text{ kJ}^2 \cdot \text{mol}^{-2}$ .



E5 has the highest  $\Delta_f H_{\text{Cond}}^{\circ}$  value (2033.37 kJ·mol<sup>-1</sup>) among all the 56 triazole derivatives. Obviously, different substituents exert diverse influences on condensed phase heats of formation. -NO<sub>2</sub>, -N<sub>3</sub>, and -NF<sub>2</sub> groups increase  $\Delta_f H_{\text{Cond}}^{\circ}$  values, and their contribution to the  $\Delta_f H_{\text{Cond}}^{\circ}$  value is in the order of -N<sub>3</sub> > -NO<sub>2</sub> > -NF<sub>2</sub>. Whereas -ONO<sub>2</sub>, and -CH(NO<sub>2</sub>)<sub>2</sub> groups lead to a small decrease in  $\Delta_f H_{\text{Cond}}^{\circ}$  values. -N<sub>3</sub> derivative is much larger than that of other derivatives, which is in agreement with previous observations that the azido group is one of the most energetic functional groups currently known.<sup>45,46</sup>

### 3.3 Energetic properties

Detonation velocity ( $D$ ) and detonation pressure ( $P$ ) are two important parameters for triazole-based high energetic compounds. Table 5 presents the predicted densities, heats of detonation, detonation velocities, detonation pressures, and oxygen balances for these compounds. For comparisons, the experimental detonation performance of known explosive RDX and HMX are also tabulated in table 5. As shown in table 5, all the substituted derivatives have relatively high  $\rho$  values. The introduction of the substituted groups greatly increases the  $\rho$  values of the unsubstituted compounds. The -NF<sub>2</sub> substituted triazole derivatives have the largest  $\rho$  values in the same series. B6 has the highest  $\rho$  value (2.20 g·cm<sup>-3</sup>) among all the 56 compounds.

The calculated heats of detonation in table 5 show that substituting -NO<sub>2</sub>, -ONO<sub>2</sub>, -N<sub>3</sub>, -NF<sub>2</sub>, and -CH(NO<sub>2</sub>)<sub>2</sub> increase the heats of detonation compared to that of the corresponding unsubstituted compounds, whereas the opposite is true for -NH<sub>2</sub>, indicating that the -NO<sub>2</sub>, -ONO<sub>2</sub>, -N<sub>3</sub>, -NF<sub>2</sub>, and -CH(NO<sub>2</sub>)<sub>2</sub> groups are helpful for increasing their heats of explosion, while the substitution of -NH<sub>2</sub> reduces their  $Q$  values. There are 19 compounds with higher  $Q$  than RDX. B3 has the highest  $Q$  value (1961.61 J·g<sup>-1</sup>) among all the compounds.

The effects of the substituents on the densities mean that the triazole derivatives have different detonation velocities, and detonation pressures. -NF<sub>2</sub> or -NO<sub>2</sub> substituted derivatives have higher detonation velocities, and detonation pressures than the other substituted ones, and the derivatives with the -NF<sub>2</sub> group have the largest  $D$  and  $P$  values ( $D > 9.80$  km·s<sup>-1</sup> and  $P > 46.00$  GPa). This shows that the substitutions of -NO<sub>2</sub> and especially -NF<sub>2</sub> are helpful for increasing the detonation properties of the triazole derivatives. Because of the low densities, the -N<sub>3</sub> substituted derivatives have the largest  $\Delta_f H_{\text{Cond}}^{\circ}$  among triazole derivatives, but their

explosive performance is not outstanding. In addition, B6 has the highest  $D$  (10.49 km·s<sup>-1</sup>) and  $P$  (54.56 GPa) values among the 56 designed compounds.

Besides, the relative positions of triazoles influence not only  $\Delta_f H_{\text{Gas}}^{\circ}$  but also the energetic properties. For instance, C3 has slightly higher density, heat of detonation, detonation velocity, and detonation pressure than E3, whereas the isomer D3 with one more N-N bond has the largest corresponding values, same as that of other isomers. Based on the above analyses, it can be concluded that -NO<sub>2</sub>, -ONO<sub>2</sub>, -N<sub>3</sub>, -NF<sub>2</sub>, and -CH(NO<sub>2</sub>)<sub>2</sub> groups are effective structural units for increasing the densities and detonation properties of triazole derivatives, especially -NO<sub>2</sub>, and -NF<sub>2</sub> structural units. In addition, the oxygen balance is another important criterion for selecting potential high energetic compounds. -NO<sub>2</sub> group is good for improving the oxygen balance. It is seen in table 5 that A3, B3, C3, D3, E3, F3, G3, and H3 have perfect oxygen balance equal to zero, that is, it does not need any atmospheric oxygen to combust and it gives off more energy during the explosion. Therefore, in the design of molecules, one shall better keep the oxygen balance equal to zero.

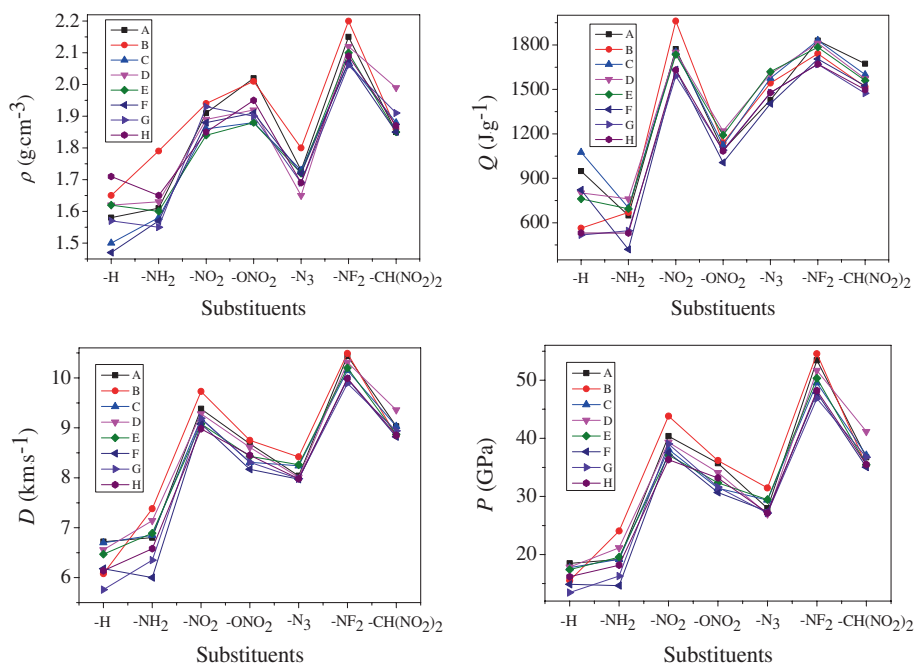
Figure 3 displays the comparison of the calculated  $\rho$ ,  $Q$ ,  $D$  and  $P$  values of triazole derivatives with different substituents. It is clear that the trend in  $\rho$  throughout the series is very similar to the trends seen for  $D$  and  $P$  in the triazole derivatives. However, some of the triazole derivatives have higher  $\rho$  values but lower  $D$  and  $P$  values than nitramine RDX or HMX. This is because their heats of detonation cause the densities to have less influence on  $D$  and  $P$ . This in turn shows that the density is not always the key factor when determining detonation properties.

Considering the quantitative criteria of high energetic compounds, that is,  $\rho \approx 1.90$  g·cm<sup>-3</sup>,  $D \approx 9.0$  km·s<sup>-1</sup>, and  $P \approx 40.0$  GPa, it is found from table 5 that series A (A3, A6), series B (B3, B6), series C (C3, C6), series D (D3, D6, D7), series E (E3, E6), series F (F3, F6), series G (G3, G6), and series H (H3, H6) satisfy the requirements. Moreover, most derivatives of A-H (A3, A6, B3, B6, C6, D3, D6, D7, E6, F6, G3, G6, H6) have better detonation properties over the famous nitramine explosive HMX ( $\rho = 1.91$  g·cm<sup>-3</sup>,  $D = 9.10$  km·s<sup>-1</sup>,  $P = 39.00$  GPa). If compared with another commonly used explosive RDX ( $\rho = 1.82$  g·cm<sup>-3</sup>,  $D = 8.75$  km·s<sup>-1</sup>,  $P = 34.00$  GPa), the triazole derivatives have much better explosive performance. Therefore, if A3, A6, B3, B6, C3, C6, D3, D6, D7, E3, E6, F3, F6, G3, G6, H3, and H6 can be synthesized, these derivatives will have better exploitable values. Thus, further investigations are still needed.

**Table 5.** Predicted densities ( $\rho$ , g·cm<sup>-3</sup>), heats of detonation ( $Q$ , J·g<sup>-1</sup>), detonation velocities ( $D$ , km·s<sup>-1</sup>), detonation pressures ( $P$ , GPa), and oxygen balance ( $OB$ , %) for the triazole derivatives.

Compd.	$OB$	$\rho$	$Q$	$D$	$P$
A1	-117.65	1.58	948.83	6.72	18.48
A2	-97.96	1.61	648.85	6.80	19.16
A3	0	1.91	1771.84	9.38	40.38
A4	16.84	2.02	1090.18	8.68	35.71
A5	-42.67	1.73	1428.06	8.04	27.97
A6		2.15	1830.47	10.44	53.43
A7	-5.80	1.85	1673.42	9.03	36.73
B1	-117.65	1.65	563.95	6.08	15.54
B2	-97.96	1.79	669.47	7.38	24.05
B3	0	1.94	1961.61	9.73	43.83
B4	16.84	2.01	1141.17	8.75	36.18
B5	-42.67	1.80	1542.04	8.42	31.47
B6		2.20	1741.03	10.49	54.56
B7	-5.80	1.86	1518.02	8.84	35.36
C1	-117.65	1.50	1075.80	6.70	17.73
C2	-97.96	1.58	701.11	6.85	19.18
C3	0	1.86	1754.08	9.18	38.10
C4	16.84	1.88	1123.97	8.31	31.41
C5	-42.67	1.73	1574.74	8.24	29.37
C6		2.07	1831.19	10.15	49.54
C7	-5.80	1.88	1600.54	9.03	37.10
D1	-117.65	1.62	801.55	6.56	17.85
D2	-97.96	1.63	760.95	7.14	21.16
D3	0	1.89	1751.36	9.28	39.31
D4	16.84	1.92	1219.43	8.61	34.12
D5	-42.67	1.65	1604.82	8.01	26.97
D6		2.12	1811.30	10.31	51.68
D7	-5.80	1.99	1570.91	9.36	41.18
E1	-117.65	1.62	761.06	6.47	17.40
E2	-97.96	1.60	695.09	6.89	19.58
E3	0	1.84	1735.86	9.08	37.09
E4	16.84	1.88	1191.50	8.43	32.34
E5	-42.67	1.72	1619.92	8.26	29.45
E6		2.10	1785.18	10.20	50.34
E7	-5.80	1.85	1559.61	8.87	35.46
F1	-117.65	1.47	822.49	6.18	14.89
F2	-97.96	1.57	420.57	6.00	14.66
F3	0	1.88	1631.78	9.08	37.54
F4	16.84	1.91	1006.40	8.17	30.68
F5	-42.67	1.72	1403.43	7.97	27.41
F6		2.07	1705.67	9.98	47.81
F7	-5.80	1.85	1523.89	8.82	35.05
G1	-117.65	1.57	518.28	5.76	13.48
G2	-97.96	1.55	546.24	6.35	16.29
G3	0	1.93	1589.30	9.19	39.04
G4	16.84	1.90	1089.55	8.31	31.59
G5	-42.67	1.69	1477.63	7.98	27.15
G6		2.06	1669.87	9.89	46.85
G7	-5.80	1.91	1473.81	8.94	36.74
H1	-117.65	1.71	531.72	6.14	16.20
H2	-97.96	1.65	530.13	6.58	18.19
H3	0	1.85	1631.07	8.98	36.34
H4	16.84	1.95	1083.96	8.45	33.19
H5	-42.67	1.69	1477.83	7.98	27.16
H6		2.09	1670.52	9.99	48.23
H7	-5.80	1.87	1498.18	8.85	35.51
RDX	-21.61	1.82 <sup>a</sup>	1590.72 <sup>a</sup>	8.75 <sup>a</sup>	34.00 <sup>a</sup>
HMX	-21.61	1.91 <sup>a</sup>	1633.87 <sup>a</sup>	9.10 <sup>a</sup>	39.00 <sup>a</sup>

<sup>a</sup> The experimental values were taken from Ref.<sup>47</sup>



**Figure 3.** Comparison of the calculated  $\rho$ ,  $Q$ ,  $D$  and  $P$  values of triazole derivatives with different substituents.

### 3.4 Thermal stability

Studies on bond dissociation energies (BDEs) are important and essential to understand the stabilities and decomposition process of the high energetic compounds. Usually, the stronger are the weakest bonds, the more stable are the high energetic compounds; that is, the stability of the energetic compounds are directly relevant to bond strength, which is commonly described by bond dissociation energy. The possible initial steps in the decomposition process are considered for the triazole derivatives by breaking the following bonds: ring-bridge, ring-NH<sub>2</sub>, ring-NO<sub>2</sub>, ring-ONO<sub>2</sub>, ring-N<sub>3</sub>, ring-NF<sub>2</sub>, ring-CH(NO<sub>2</sub>)<sub>2</sub>, and C-NO<sub>2</sub> for -CH(NO<sub>2</sub>)<sub>2</sub> derivatives. The weakest bond among the same type of bonds is selected as the trigger bond.

The BDEs of relatively weak bonds of the triazole derivatives are listed in table 6. It was found that different substituents have different effects on the BDEs for the title compounds. For the A series, ring-bridge N-N bonds of A1, A2, A3, A4, A5, A7 may be the trigger bond for initiation of the thermolysis process. The N-F bond in the -NF<sub>2</sub> substituted compound (A6) has smaller BDE value than that of corresponding ring-bridge N-N bond. Therefore, we can infer that the trigger bond is N-F in the -NF<sub>2</sub> substituted compound. However, for the B series, ring-NH<sub>2</sub>, ring-NO<sub>2</sub>, ring-ONO<sub>2</sub>, ring-N<sub>3</sub>, ring-NF<sub>2</sub>, and C-N bond in the -CH(NO<sub>2</sub>)<sub>2</sub> substituted compound have smaller BDE values than that of corresponding ring-bridge C-C bonds. Moreover, this case is consistent with that of

the D, E, G, and H series. It is interesting to note that the N-NO<sub>2</sub> bond in -NO<sub>2</sub> substituted compound (C3) and C-NO<sub>2</sub> bond in the -CH(NO<sub>2</sub>)<sub>2</sub> substituted compound (C7) have a higher BDE than the N-N bonds of ring-bridge. This also holds for the F series.

Obviously, the same substituent exerts diverse influences on the unsubstituted compound. For example, in the B, D, E, G, and H series, -NF<sub>2</sub> group increases the BDE values, and the contribution to the BDE value is in the order of B > G > H > E > D. Most of the weakest bonds in the triazole derivatives have a relatively high BDE values. Considering the practical requirements, a quantitative criteria associated stability (BDE of the trigger bond) requirements, *i.e.*, BDE ≈ 80–120 kJ·mol<sup>-1</sup>,<sup>48</sup> is proposed and recommended for potential energetic compounds.<sup>49</sup> The calculated BDEs of triazole derivatives essentially satisfy this requirement obtained at the B3LYP/6-311G(d,p) level, which means that these compounds suffice the stability requirement of explosives.

As is well-known, a good nitrogen-rich high energetic compound not only has excellent detonation properties but also good stability. Considering the energetic properties and thermal stability, it can be concluded that series A (-NO<sub>2</sub>, -NF<sub>2</sub>, -CH(NO<sub>2</sub>)<sub>2</sub>), series B (-NO<sub>2</sub>, -NF<sub>2</sub>), series C (-NO<sub>2</sub>, -NF<sub>2</sub>, -CH(NO<sub>2</sub>)<sub>2</sub>), series D (-NO<sub>2</sub>, -NF<sub>2</sub>, -CH(NO<sub>2</sub>)<sub>2</sub>), series E (-NO<sub>2</sub>, -NF<sub>2</sub>), series F (-NO<sub>2</sub>, -NF<sub>2</sub>), series G (-NO<sub>2</sub>, -NF<sub>2</sub>, -CH(NO<sub>2</sub>)<sub>2</sub>), and series H (-NO<sub>2</sub>, -NF<sub>2</sub>) possess better energetic properties and thermal stabilities. Therefore, these 20 compounds can be considered as potential

**Table 6.** Bond dissociation energies (kJ·mol<sup>-1</sup>) of the relatively weak bonds of the triazole derivatives.

Compd.	ring-bridge	ring-NH <sub>2</sub>	ring-NO <sub>2</sub>	ring-ONO <sub>2</sub>	ring-N <sub>3</sub>	ring-NF <sub>2</sub>	ring-CH(NO <sub>2</sub> ) <sub>2</sub>	C-NO <sub>2</sub>
A1	204.42							
A2	127.42	342.06						
A3	98.18		109.83					
A4	108.47			313.26				
A5	117.76				368.18			
A6	169.97					140.28		
A7	81.46						224.06	114.96
B1	544.14							
B2	462.64	85.50						
B3	92.06		87.81					
B4	496.46			103.67				
B5	472.78				170.73			
B6	466.63					150.49		
B7	532.26						326.77	116.15
C1	286.81							
C2	80.33	415.33						
C3	267.63		211.88					
C4	199.60			375.80				
C5	90.82				324.62			
C6	180.11					234.31		
C7	273.45						442.53	104.70
D1	532.64							
D2	535.81	147.40						
D3	445.01		162.84					
D4	520.51			123.44				
D5	548.43				136.73			
D6	486.96					95.44		
D7	529.78						356.39	104.96
E1	539.95							
E2	561.51	188.06						
E3	511.27		134.07					
E4	538.81			389.36				
E5	522.96				107.39			
E6	522.08					126.00		
E7	512.48						316.52	83.97
F1	298.48							
F2	80.65	436.04						
F3	227.39		191.00					
F4	126.56			377.47				
F5	105.07				354.73			
F6	172.42					229.97		
F7	271.97						434.05	116.27
G1	534.16							
G2	506.54	199.30						
G3	465.46		112.21					
G4	514.89			91.65				
G5	510.62				141.75			
G6	499.84					133.22		
G7	524.24						362.64	123.30
H1	509.67							
H2	522.42	221.18						
H3	514.49		110.81					
H4	504.96			162.72				
H5	524.90				141.49			
H6	523.16					129.87		
H7	514.57						341.24	108.53

candidates for nitrogen-rich high energetic compounds with enhanced performance and reduced sensitivity.

#### 4. Conclusions

In this study, systematic calculations have been performed on triazole-based compounds at the DFT-B3LYP/6-311G(d,p) level. On the basis of the theoretical studies of the structures and the properties for the triazole derivatives, the following conclusions are drawn.

(1) The symmetry and hyperconjugation system existing in triazole derivatives have identical contribution to the stabilization. The HOMO and LUMO energy levels decrease when  $-\text{NO}_2$ ,  $-\text{ONO}_2$ ,  $-\text{NF}_2$ , and  $-\text{CH}(\text{NO}_2)_2$  groups are attached to the ring. The electron withdrawing groups break the  $\pi$  electron cloud system, which increases the energies of triazole derivatives. However, because of the electron donating effect, the introduction of  $-\text{NH}_2$  group will make  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  increase gradually. This shows that the HOMO and LUMO energies are associated with the substituents in the parent ring.

(2) The calculated heats of formation in condensed phase show the same trend as the heats of formation in gas phase. Moreover, the substitution of  $-\text{N}_3$  plays a very important role in increasing the heats of formation in gas phase and in condensed phase of the derivatives, while the substitution of  $-\text{ONO}_2$  group greatly reduces the values. The energy-rich bonds in  $-\text{N}_3$  group release large amount of energy, which increases the heats of formation in gas phase and in condensed phase.

(3) Most of the substituents improve  $\rho$ ,  $D$ , and  $P$  values. The substitutions of  $-\text{NO}_2$  and especially  $-\text{NF}_2$  are very helpful for increasing the densities, detonation properties of the triazole derivatives. Calculated results of detonation velocities and detonation pressures for triazole derivatives indicate that series A (A3, A6), series B (B3, B6), series C (C3, C6), series D (D3, D6, D7), series E (E3, E6), series F (F3, F6), series G (G3, G6), and series H (H3, H6) satisfy the quantitative criteria for nitrogen-rich high energetic compounds.

(4) An analysis of the BDEs for several relatively weak bonds suggests that most of the triazole derivatives have good thermal stabilities. In addition, because of the inductive effect of different substituents, the thermal stabilities of the triazole derivatives decrease.

(5) Considering the energetic properties and thermal stability, series A ( $-\text{NO}_2$ ,  $-\text{NF}_2$ ,  $-\text{CH}(\text{NO}_2)_2$ ), series B ( $-\text{NO}_2$ ,  $-\text{NF}_2$ ), series C ( $-\text{NO}_2$ ,  $-\text{NF}_2$ ,  $-\text{CH}(\text{NO}_2)_2$ ), series D ( $-\text{NO}_2$ ,  $-\text{NF}_2$ ,  $-\text{CH}(\text{NO}_2)_2$ ), series E ( $-\text{NO}_2$ ,  $-\text{NF}_2$ ), series F ( $-\text{NO}_2$ ,  $-\text{NF}_2$ ), series G ( $-\text{NO}_2$ ,  $-\text{NF}_2$ ),

$-\text{CH}(\text{NO}_2)_2$ ), and series H ( $-\text{NO}_2$ ,  $-\text{NF}_2$ ) can be considered as potential candidates for nitrogen-rich triazole-based high energetic compounds with higher performance and thermal stability. These results provide theoretical support for molecular design and experimental synthesis of novel triazole-based high energetic compounds.

#### Acknowledgments

This work was supported by the Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi and Natural Science Foundation of Shanxi Normal University (Grant No. ZR1504).

#### References

- Klapotke T M and Witkowski T G 2015 *Propell. Explos. Pyrot.* **40** 366
- Fischer D, Klapotke T M and Stierstorfer J 2015 *Angew. Chem. Int. Ed.* **54** 10299
- Yedukondalu N and Vaitheeswaran G 2015 *J. Chem. Phys.* **143** 064508
- Wei H, He C L, Zhang J H and Shreeve J M 2015 *Angew. Chem. Int. Ed.* **54** 9367
- Piercey D G, Chavez D E, Heimsch S, Kirst C, Klapotke T M and Stierstorfer J 2015 *Propell. Explos. Pyrot.* **40** 491
- Wu J T, Zhang J G, Yin X, Cheng Z Y and Xu C X 2015 *New J. Chem.* **39** 5265
- Klapotke T M, Schmid P C, Schnell S and Stierstorfer J 2015 *J. Mater. Chem. A* **3** 2658
- Guo Y X, Feng X, Han T Y, Wang S, Lin Z G, Dong Y P and Wang B 2014 *J. Am. Chem. Soc.* **136** 15485
- Becuwe A and Delclos A 1989 *Proceedings of the Ninth International Symposium on Detonation* (Arlington, VA: Office of the Chief of Naval Research) pp. 1008–1013
- Singh G, Kapoor I P S, Tiwari S K and Felix P S 2001 *J. Hazard. Mater.* **81** 67
- Lee J S and Jaw K S 2006 *J. Therm. Anal. Calorim.* **85** 463
- Dippold A A, Klapotke T M, Martin F A and Wiedbrauk S 2012 *Eur. J. Inorg. Chem.* 2429
- Watenberg C, Charne P and Laval F 1995 *Propell. Explos. Pyrot.* **20** 23
- Tang Y X, Gao H X, Parrish D A and Shreeve J M 2015 *Chem. Eur. J.* **21** 11401
- Wu Q, Zhu W H and Xiao H M 2014 *J. Mol. Model.* **20** 2441
- Tang Y X, Yang H W, Wu B, Ju X H, Lv C X and Cheng G B 2013 *Angew. Chem. Int. Ed.* **52** 1
- Klapotke T M, Schmid P C, Schnell S and Stierstorfer J 2015 *Chem. Eur. J.* **21** 9219
- Bian C M, Wang K, Liang L X, Zhang M, Li C and Zhou Z M 2014 *Eur. J. Inorg. Chem.* 6022
- Srinivas D, Ghule V D and Muralidharan K 2014 *RSC Adv.* **4** 7041
- He P, Zhang J G, Wang K, Yin X, Jin X and Zhang T L 2015 *Phys. Chem. Chem. Phys.* **17** 5840
- Li X H and Zhang R Z 2014 *J. Chem. Sci.* **126** 1753



22. Zhao G Z and Lu M 2013 *J. Mol. Model.* **19** 3403
23. Singh R, Singh H J and Sengupta S K 2015 *J. Chem. Sci.* **127** 1099
24. Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Scalmani G, Barone V, Mennucci B, Petersson G A, Nakatsuji H, Caricato M, Li X, Hratchian H P, Izmaylov A F, Bloino J, Zheng G, Sonnenberg J L, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery J A, Peralta J E, Ogliaro F, Bearpark M, Heyd J J, Brothers E, Kudin K N, Staroverov V N, Keith T, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant J C, Iyengar S S, Tomasi J, Cossi M, Rega N, Millam J M, Klene M, Knox J E, Cross J B, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Martin R L, Morokuma K, Zakrzewski V G, Voth G A, Salvador P, Dannenberg J J, Dapprich S, Daniels A D, Farkas O, Foresman J B, Ortiz J V, Cioslowski J and Fox D J 2010 *Gaussian 09, Revision C. 01* (Wallingford, CT: Gaussian Inc.)
25. Politzer P, Martinez J, Murray J S, Concha M C and Toro-Labbé A 2009 *Mol. Phys.* **107** 2095
26. Becke A D 1992 *J. Chem. Phys.* **97** 9173
27. Lee C, Yang W and Parr R G 1988 *Phys. Rev. B* **37** 785
28. Zhao G Z and Lu M 2013 *Struct. Chem.* **24** 139
29. Vo T T, Zhang J H, Parrish D A, Twamley B and Shreeve J M 2013 *J. Am. Chem. Soc.* **135** 11787
30. Atkins P W 1982 In *Physical Chemistry* 2nd ed. (Oxford: Oxford University Press)
31. Rice B M, Pai S V and Hare J 1999 *Combust. Flame* **118** 445
32. Politzer P, Lane P and Murray J S 2011 *Cent. Eur. J. Energetic Mater.* **8** 39
33. Politzer P, Ma Y, Lane P and Concha M C 2005 *Int. J. Quantum Chem.* **105** 341
34. Kamlet M J and Jacobs S J 1968 *J. Chem. Phys.* **48** 23
35. Zhang X H and Yun Z H 1989 In *Explosive Chemistry* (Beijing: National Defence Industry Press)
36. Liu H, Wang F, Wang G X and Gong X D 2012 *J. Comput. Chem.* **33** 1790
37. Li J S 2010 *J. Phys. Chem. B* **114** 2198
38. Cao X Z, Song T Y and Wang X Q 1987 In *Inorganic Chemistry* (Beijing: Higher Education Press)
39. Scott A P and Radom L 1996 *J. Phys. Chem.* **100** 16502
40. Dean J A 1999 In *Lange's Handbook of Chemistry* 15th ed. (New York: McGraw-Hill)
41. David R L 2003–2004 In *Handbook of Chemistry and Physics* 84th ed. (Boca Raton: CRC Press)
42. Afeefy H Y, Liebman J F and Stein S E 2000 *NIST Chemistry WebBook: NIST Standard Reference Database Number 69* (Gaithersburg: National Institute of Standards and Technology)
43. Yong P, Zhu W H and Xiao H M 2012 *J. Mol. Model.* **18** 3125
44. Wei T, Zhang J J, Zhu W H, Zhang X W and Xiao H M 2010 *J. Struct. Chem.: (THEOCHEM)* **956** 55
45. Huynh M H V, Hiskey M A, Chavez D E, Naud D L and Gilardi R D 2005 *J. Am. Chem. Soc.* **127** 12537
46. Chavez D E, Hiskey M A and Gilardi R D 2000 *Angew. Chem. Int. Ed.* **39** 1791
47. Talawar M B, Sivabalan R, Mukundan T, Muthurajan H, Sikder A K, Gandhe B R and Subhananda R 2009 *J. Hazard. Mater.* **161** 589
48. Chung G, Schmidt M W and Gordon M S 2000 *J. Phys. Chem. A* **104** 5647
49. Xiao H M, Xu X J and Qiu L 2008 In *Theoretical Design of High Energy Density Materials* (Beijing: Science Press)